



Electrochemical-driven water splitting catalyzed by a water-soluble cobalt(II) complex supported by N,N'-bis(2'-pyridinecarboxamide)-1,2-benzene with high turnover frequency



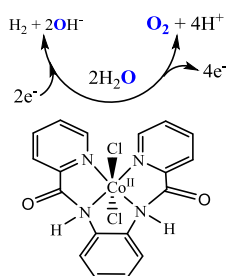
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HIGHLIGHTS

- [Co(bpbH₂)Cl₂] **1** can catalyze both water oxidation and reduction to provide O₂ and H₂, respectively.
- Water reduction occurs with a TOF of 376 mol h⁻¹ at an overpotential of 687.6 mV (pH 7.0).
- Water oxidation occurs at an overpotential of 560 mV to give O₂ with a TOF of ~81.54 s⁻¹ (pH 8.6, the lowest pH).

GRAPHICAL ABSTRACT



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ABSTRACT

The oxidation and reduction of water is a key challenge in the production of chemical fuels from electricity. Reported here is a soluble cobalt (II) complex, [Co(bpbH₂)Cl₂] **1** (bpbH₂: N,N'-bis(2'-pyridinecarboxamide)-1,2-benzene), a highly active homogeneous electrocatalyst for both electrolytic water oxidation and reduction in purely aqueous solution. Electrochemical studies indicate that the catalyst is a water-soluble molecular species, that is among the most rapid homogeneous catalysts for water oxidation, with a turnover frequency of ~81.54 s⁻¹ (at pH 8.6, the lowest pH among those of any reported electrocatalysts) at an overpotential of 560 mV. **1** also can catalyze hydrogen evolution from water with a TOF of 376 mol of hydrogen per mole of catalyst per hour at an overpotential of 687.6 mV (pH 7.0). This is attributed to the planar ligand (bpbH₂), that coordinates strongly through four nitrogen atoms to the cobalt center, leaving two Cl⁻ ions in axial position and making the Cl⁻ ion ionize in organic solvents or water, and can stabilize both the high and low oxidation states of cobalt well.

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1. Introduction

Water is the only waste-free electron-source substrate that could sustain the scale (multibillion tonnes) of the process required to supply our energy demands. Thus, splitting water into hydrogen and oxygen is one of the most attractive scenarios for

solar energy harvesting and sustainable energy production [1–6]. However, the kinetically slow oxygen evolution reaction (OER) $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$ (in acid) or $4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^-$ (in base) represents a significant efficiency loss in water-splitting systems [7,8]. Currently, one of the key challenges to water splitting is the development of efficient catalysts for the water oxidation and reduction reactions with low overpotentials, good stability, and high turnover rates [9,10]. Many research groups, including ours, have focused on the development of molecular

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catalysts employing more abundant metals, and several complexes that contain nickel [11,12], cobalt [13–17], iron [18–20], copper [21–26] and molybdenum [27–31] have been developed as electrocatalysts for the reduction of water to form H₂. Another notable progress has been made in homogeneous water oxidation catalysis with transition metal complexes, including cobalt [32–34], copper [35,36] and iron [37–43]. Despite much progress in water oxidation and reduction catalysis, major improvements in several areas, including lowering overpotentials, increasing catalyst durability, and using earth-abundant elements, are needed before efficient electrocatalytic water splitting can be realized. Especially, high pH severely limits their practical utility. To the best of our knowledge, there have been few complexes reported in the literature that can function efficiently as both water oxidation catalysts (WOCs) and water reduction catalysts (WRCs). This is because WOCs and WRCs require different ligands to support. Efficient WOCs generally are in the form of metal oxides [44] or with oxidation-resistant ligands [45,46], while efficient WRCs prefer softer ligands to generate low-valent active intermediates that can reduce protons at low over-potentials, such as oxime [47–50], and phosphine [51] ligands. As a continuous work [52,53], reported here is a water-soluble cobalt(II) electrocatalyst, [Co(bpbH₂)Cl₂] **1** that can catalyze both water oxidation with a TOF of ~81.54 s⁻¹ at pH 8.6 and reduction with a TOF of 376 mol of hydrogen per mole of catalyst per hour at an overpotential of 687.6 mV (pH 7.0). We hope this can open a new direction in water oxidation and reduction catalysis using inexpensive and earth-abundant materials in purely aqueous media.

2. Experimental

All commercially available reagents were used as received without further purification. Cyclic voltammograms were obtained on a CHI-660E electrochemical analyzer under oxygen-free conditions using a three-electrode cell in which a glassy carbon electrode GC was the working electrode, a saturated Ag/AgCl electrode was the reference electrode, and platinum wire was the auxiliary electrode. Controlled-potential electrolysis (CPE) in aqueous media was conducted using an air-tight glass double compartment cell

separated by a glass frit. The working compartment was fitted with a glassy carbon plate or an ITO plate and an Ag/AgCl reference electrode. The auxiliary compartment was fitted with a Pt gauze electrode. The working compartment was filled with 50 mL of 0.25 M buffer at different pH values, while the auxiliary compartment was filled with 35 mL phosphate buffer solution. Adding cobalt complex, both compartments were sparged for 1 h with nitrogen and cyclic voltammograms were recorded as controls. After electrolysis, a 0.5 mL aliquot of the headspace was removed and replaced with 0.5 mL of CH₄. A sample of the headspace was injected into the gas chromatograph (GC). GC experiments were carried out with an Agilent Technologies 7890A gas chromatography instrument. UV–Vis spectra were measured on a Hitachi U-3010. ESI-MS experiment was performed on a Bruker Daltonics Esquire 3000 Spectrometer by introducing samples directly into the ESI source using a syringe pump.

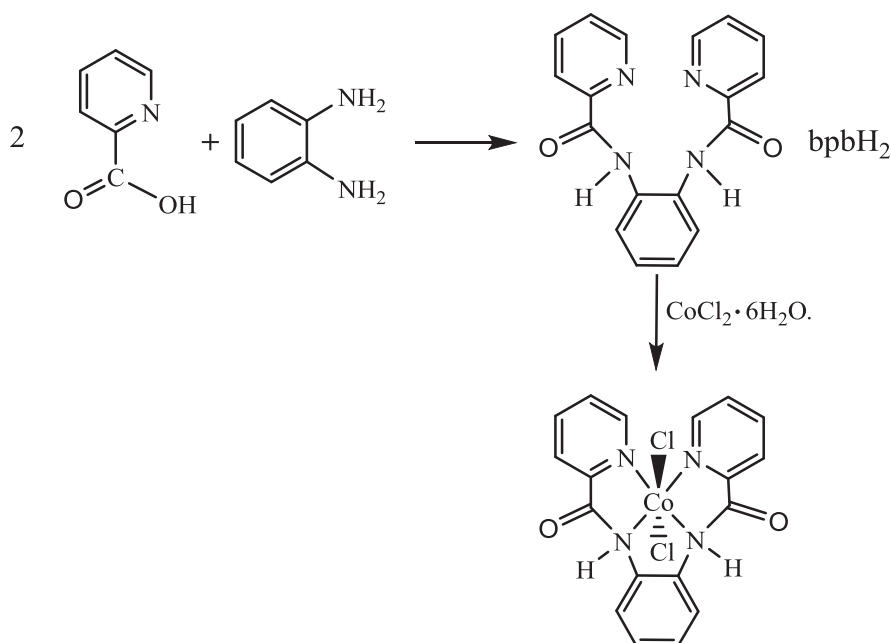
3. Results and discussion

3.1. General characterization

According to the literature [54], the reaction of CoCl₂ and bpbH₂ provides a cobalt(II) complex, [Co(bpbH₂)Cl₂] **1** (Scheme 1), which is in agreement with the result of ESI-MS analysis. The electrospray mass spectrum of **1** exhibits one ion at a mass-to-charge ratio (*m/z*) of 508.1207, with mass and isotope distribution pattern corresponding to [Co(bpbH₂)Cl₂·2H₂O-Na-H]⁺ (calculated *m/z* of 508.18) (Fig. S1). **1** is very soluble in water and organic solvents, such as methanol and ethanol. The UV–vis spectrum of the title complex was recorded in aqueous solution, with a main feature at 500 nm, which corresponds to a d–d transition of cobalt ion (Fig. S2). The UV–vis spectra of **1** in buffered aqueous solutions in pH 5.4–10.6 exhibit similar peaks to those in water (Fig. S3). Therefore, we can explore its electrochemical properties in pH 5.4–10.6.

3.2. Electrochemical studies

From Fig. 1, in DMF solution at a glassy carbon electrode, the cobalt complex displays one reversible Co^{II}/Co^I redox couple at E₁



Scheme 1. Schematic representation of the synthesis of [Co(bpbH₂)Cl₂].

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